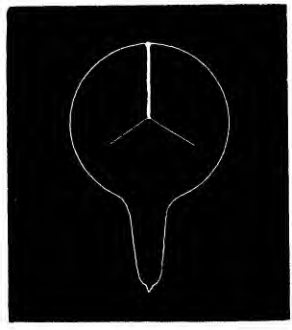
Fig. 5.



From this experience I think we may consider that at an exhaustion of a millionth of an atmosphere, air is an absolute non-conductor of statical electricity. It is, therefore, legitimate to conclude that the vacuum of interstellar space offers equal obstruction to the discharge of electrified bodies, without necessarily interfering with their mutual repulsion if similarly electrified. It is possible that in these facts an explanation may be found of some obscure celestial phenomena.

II. "On the Reversal of the Lines of Metallic Vapours." No. IV.

By G. D. Liveing, M.A., Professor of Chemistry, and J. Dewar, M.A., F.R.S., Jacksonian Professor, University of Cambridge. Received February 12, 1879.

In the experiments described in the following communication, instead of introducing the substances to be observed in the metallic form into our tubes, we have endeavoured to overcome, to some extent, the difficulty of the presence of impurities by making use of reactions which should generate the metallic vapours within the tubes. For this purpose we have generally employed the great reducing power of carbon and of aluminium at high temperatures.

In a former communication ("Proc. Roy. Soc.," vol. xxvii) we described the reversal of the two blue lines of cæsium and the two violet lines of rubidium by the vapours of those metals, produced by heating their chlorides with sodium in glass tubes. It might be doubtful from these experiments whether the absorption were due to the metals or to the chlorides. To decide this question, we first tried cæsium chloride by itself, heated in a tube such as we used before. No absorption lines could be seen, although a good deal of the chloride had been vaporized and distilled to the cool part of the tube. The experiments were next repeated, both with rubidium and cæsium

chlorides along with metallic lithium. The two violet lines of rubidium and the two blue lines of cæsium were reversed, as when sodium was used instead of lithium, and as the lithium gave no sensible vapour, the observations could easily be continued for a much longer time with the same tubes. No other absorption lines could be discerned. It may be observed, however, that it is not easy to obtain a source of light sufficiently rich in the least refrangible red to allow of observations on the absorption of light so little refrangible as the red rubidium lines. A platinum wire, heated nearly to fusion by an electric current, appeared to give the brightest light in this part of the spectrum, but of that light no definite absorption by the rubidium could be observed in the red. We then had some mixtures of carbonate of cæsium with carbon, and of carbonate of rubidium with carbon, prepared by charring the tartrates; and observed the results of heating these mixtures in narrow porcelain tubes, placed vertically in a furnace, as described in our first communication on this subject ("Proc. Roy. Soc.," vol. xxvii). A small quantity of the cæsium mixture, introduced into a tube at a bright red heat, showed instantly the two blue lines reversed and so much expanded as to be almost in contact. The width of the dark lines decreased as the cæsium evaporated, but they remained quite distinct for a very long time. A similar effect was produced by the rubidium mixture, only it was necessary to have the tube very much hotter, in order to get enough of violet light to see the reversal of the rubidium lines. In this case the two lines were so much expanded as to form one broad dark band, which gradually resolved itself into two as the rubidium evaporated. The reversal of these lines of cæsium and rubidium seems to take place almost or quite as readily as that of the D lines by sodium, and the vapours of those metals must be extremely opaque to the light of the refrangibility absorbed, for the absorption was conspicuous when only very minute quantities of the metals were present. The red, yellow, and green parts of the spectrum were carefully searched for absorption lines, but none due to cæsium or rubidium could be detected in any case. It is perhaps worthy of remark that the liberation of such extremely electro-positive elements as cæsium and rubidium from their chlorides by sodium and by lithium, though it is probably only partial, is a proof, if proof were wanting, that so-called chemical affinity only takes a part in determining the grouping of the elements in such mixtures; and it is probable that the equilibrium arrived at in any such case is a dynamical or mobile equilibrium, continually varying with change of temperature.

Our next experiments were with charred cream of tartar in iron tubes, arranged as before. In this case a broad absorption band appeared, extending over the space from about wave-length 5,700 to 5,775, and in some cases still wider, with edges ill-defined, especially the more refrangible edge. By placing the charred cream of tartar in

the tube before it was introduced into the furnace, and watching the increase of light as the tube got hot, this band was at first seen bright on a less bright background, it gradually faded, and then came out again reversed, and remained so. No very high temperature was required for this, but a rise of temperature had the effect of widening the band. Besides this absorption, there appeared a very indefinite faint absorption in the red, with the centre at a wave-length of about 6,100, and a dark band, with a tolerably well-defined edge on the less refrangible side, at about a wave-length of 4,850, shading away towards the violet. A fainter dark band was sometimes seen beyond, with a wave-length of about 4,645; but sometimes the light seemed abruptly terminated at about wave-length 4,850. It will be noticed that these absorptions are not the same as those seen when potassium is heated in hydrogen, nor do they correspond with known emission lines of potassium, although the first, which is also the most conspicuous and regularly visible of these absorptions, is very near a group of three bright lines of potassium. It seemed probable that they might be due to a combination of potassium with carbonic oxide. We tried the effect of heating potassium in carbonic oxide in glass tubes, but, though the potassium united readily with the gas, the compound did not appear to volatilize at a dull red heat, and no absorption, not even that which potassium gives when heated in nitrogen under similar circumstances, could be seen. We then tried induction sparks between an electrode of potassium and one of platinum in an atmosphere of carbonic oxide. The usual bright lines of potassium were seen, and also a bright band, identical in position with the above-mentioned band, between wave-lengths about 5,700 and 5,775. This band could not be seen when hydrogen was substituted for carbonic oxide. A mixture of sodium carbonate and charred sugar, heated in an iron tube, gave only the same absorption as sodium in hydrogen. There were also no indications of any absorption due to a compound of rubidium or of cæsium with carbonic oxide.

The experiments of Mallet ("Chem. Soc. J.," 1876) on the volatility of calcium, strontium, and barium, and the reducing action of aluminium on the oxides, especially in the presence of carbonate of sodium, induced us to try similar mixtures in our tubes.

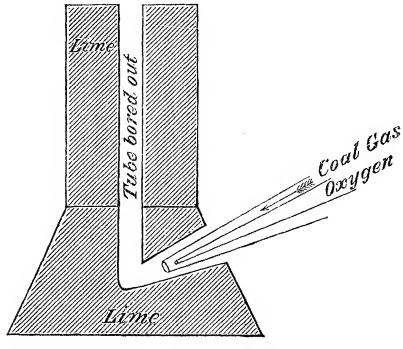
A mixture of barium carbonate, aluminium filings, and lamp-black, heated in a porcelain tube, gave two absorption lines in the green, corresponding in position to bright lines seen when sparks are taken from a solution of barium chloride, at wave-lengths 5,242 and 5,136, marked α and β by Lecoq de Boisbaudran. These two absorptions were very persistent, and were produced on several occasions. A third absorption line, corresponding to line δ of Boisbaudran, was sometimes seen, and on one occasion, when the temperature was as high as could be obtained in the furnace fed with Welsh coal, and a

mixture of charred barium tartrate with aluminium was used, a fourth dark line was seen with wave-length 5,535. This line was very fine and sharply defined, whereas the other three lines were ill-defined at the edges; it is, moreover, the only one of the four which corresponds to a bright line of metallic barium.

Repeated experiments with charred tartrates of calcium and of strontium mixed with aluminium gave no results, but on one occasion, when some sodium carbonate was used along with the charred tartrate of strontium and aluminium, the blue line of strontium was seen reversed, and on another occasion, when a mixture of charred potassium, calcium, and strontium tartrates, and aluminium was used, the calcium line, with wave-length 4,226, was seen reversed. The fire in this case was fed with gas retort carbon, and the temperature such that iron tubes, though well coated with fire-clay, gave way in a few minutes. It appears, therefore, that the blue line of strontium, and the above-mentioned violet line of calcium, are reversible by this method, but not so easily or so certainly as the lines of barium or its compounds above mentioned.

In order to obtain higher temperatures than we could obtain in the furnace used in our former experiments, we have made preliminary experiments with lime crucibles heated (1) by a jet of coal-gas and oxygen; (2) by the electric arc. For this purpose a block of chalk or lime had a vertical tubular hole bored into it about 6 or 7 millims. in diameter, and for the gas jet a second lateral boring, meeting the other boring at the bottom (fig. 1). For the electric arc two lateral

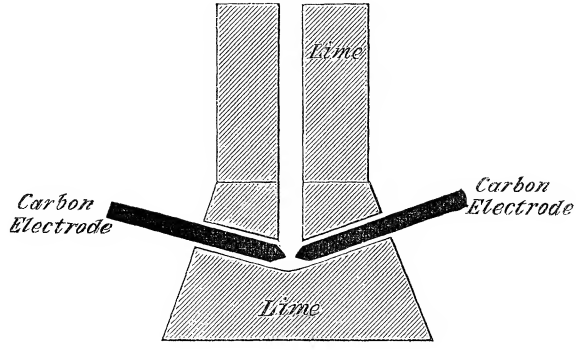
Fig. 1.



borings are made on opposite sides of the block, meeting the vertical boring at its bottom (fig. 2). Above the crucible we place a mirror inclined at 45°, so as to reflect the light from the vertical boring on to the slit of a spectroscope, a plate of mica being interposed between the mirror and crucible to deflect the stream of hot gas and

catch the smoke, which would otherwise soon dim the surface of the mirror.

Fig. 2.



With the jet of coal-gas and oxygen the usual green and orange bands of lime and the violet line of calcium (wave-length 4,226) were seen bright on the continuous spectrum, and on dropping in some aluminium their brightness increased at the same time that a dark line appeared in the middle of both the orange and green band. This dark line speedily disappeared in the case of the orange band, but lasted longer in the green band. When some lithium carbonate was put into the crucible and the coal-gas turned on so as to be in excess, the red lithium line was reversed, appearing slightly expanded with a black line down the middle.

For the electric arc 25 Grove's cells were used, and the carbon poles introduced through the lateral openings, so as to meet at the bottom of the vertical boring of the lime crucible. A very brilliant spectrum of bright lines was produced on bringing the poles in contact, while a copious stream of vapours ascended the tube. On drawing apart the poles, which could be done for nearly an inch without stopping the current, the calcium line (wave-length 4,226) was seen reversed. On dropping some aluminium into the crucible the calcium line just mentioned was very much expanded, and appeared with a broad black line in the middle. The other calcium lines in the neighbourhood on the less refrangible side were also expanded considerably, but were not seen reversed. The more refrangible lines (Fraunhofer's H), however, remained sharply defined, and did not appear sensibly expanded or reversed.

On introducing some strontia the blue strontium line (wave-length 4,607) was immediately seen reversed, appearing as a broadish bright band, with a dark line in the middle. There were no indications of the reversal of any other strontium line, though the more refrangible lines were conspicuously bright.

When lithium carbonate was introduced the red line was at once seen reversed, but not much expanded. When some aluminium was added, the lithium blue line (wave-length 4,604) was seen with a dark line in the middle for a short time only. The green line of lithium was very bright indeed, and appeared somewhat expanded on the addition of aluminium, but showed no reversal.

On putting some baryta into the crucible the line with wave-length 5,535 was reversed, appearing very black but narrow. No other barium line could be seen reversed in that crucible, but in another crucible into which magnesia had been introduced, a dark line, with wave-length about 4,930, was observed, which may probably be ascribed to barium.

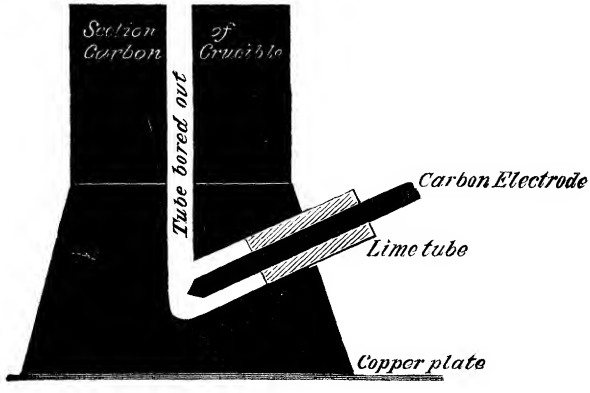
With magnesia and aluminium the least refrangible of the *b* group was seen reversed, all the *b* group being expanded.

When silver was introduced, on drawing the poles apart, both the brightest green lines (wave-lengths 5,464 and 5,209) were seen for a short time with a black line down the middle.

Frequently on parting the poles, whatever might be the substance in the crucible, the whole of the brightest part of the spectrum, from the orange to the blue, appeared filled with dark lines, all equidistant and equally dark, like a fine grating. With a high dispersion these lines are seen to be ill-defined at the edges. We can only suppose them to be a banded spectrum of some compound of carbon.

The lime crucibles are very quickly destroyed, but we hope to get some more compact lime than we have hitherto had, and to employ a more powerful electric current. The use of carbon or magnesia for crucibles will, we anticipate, enable experiments of this kind to be extended much further, and applied to various reactions taking place at the temperature of the arc. In the case of carbon crucibles the block of carbon itself will form one electrode, the other electrode

Fig. 3.



passing through a tube of lime as in (fig. 3). It is our intention to try a combination of the electric arc and induction spark in these crucibles. It is hardly necessary to note that the projection of the reversals of the lines of metallic vapours may be effected by this method better than by any method heretofore in use.

February 27, 1879.

THE PRESIDENT in the Chair.

The Presents received were laid on the table, and thanks ordered for them.

Major-General Thuillier (elected 1869) was admitted into the Society.

The following Papers were read:—

I. "Studies in Acoustics. I. On the Synthetic Examination of Vowel Sounds." By WILLIAM HENRY PREECE and AUGUSTUS STROH. Communicated by the PRESIDENT. Received February 17, 1879.

[PLATES 6, 7.]

1. The authors of this paper have devoted much time during the past twelve months to a study of sonorous vibrations and the reproduction of speech. The invention of the phonograph has proved a great stimulus to this study. Many have worked in the same field, and many of the facts elicited by the authors have been anticipated by those who have been able to give more continuous study to the subject. Nevertheless, the mode of enquiry, the apparatus employed, and the results obtained are thought to be of sufficient novelty to justify their being brought before the Royal Society.

2. The curves traced by the vibrating disk of the phonograph on tinfoil, whether examined microscopically or reproduced by a species of pantelograph, were soon found to be insufficiently delicate to give the nicer shades of sound, and to fail to indicate the true curve of vibrations in all cases. This is shown by the imperfect reproduction of speech by the phonograph itself; the merging of the labial and dental sounds into one another, and the absence of all the sibilants and generally of the "noises" of speech. The phonograph is in reality a very imperfect speaker, and it requires the aid of much imagination and considerable guessing to follow its reproductions. It produces

FIG. 2.

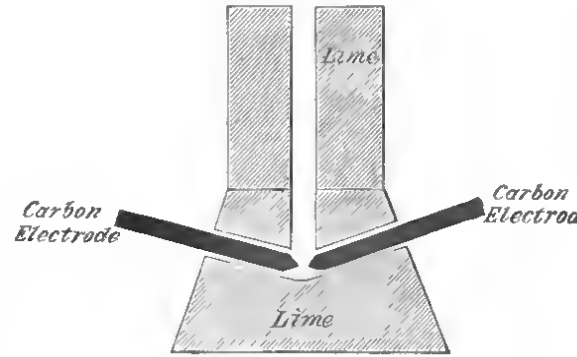
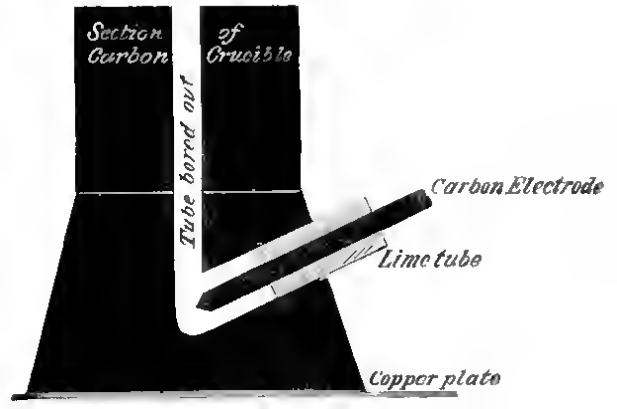


FIG. 3.


Section of Carbon Crucible
Tube bored out
Carbon Electrode
Lime tube
Copper plate